

---

# (12) UK Patent Application (19) GB (11) 2 167 758A

(43) Application published 4 Jun 1986

(21) Application No 8525099	(51) INT CL <sup>4</sup> C12N 9/98
(22) Date of filing 11 Oct 1985	(52) Domestic classification (Edition H) C3H K4 U1S 1376 1452 C3H
(30) Priority data	(56) Documents cited None
(31) 59/213669      (32) 12 Oct 1984      (33) JP	(58) Field of search C3H Selected US specifications from IPC sub-class C12K C12N
(71) Applicant Showa Denko Kabushiki Kaisha (Japan), No. 13-9 Shibadaimon 1-chome, Minato-ku, Tokyo, Japan	
(72) Inventors Hitoshi Iijima, Masayuki Nishinaka	
(74) Agent and/or address for service Marks & Clerk, Alpha Tower, Suffolk Street Queensway, Birmingham B1 1TT	

---

**(54) Enzyme-granulating method and granular composition containing enzyme**

(57) The method comprises supplying a granulator with a feed composition comprising 1 to 35% by weight of an enzyme and from 0.5 to 30% by weight of a synthetic fiber chip or pulp, with the balance being an extender or filler, shaping the supplied feed composition into granules and drying said granules. The granulated enzyme product has improved stability and enhanced strength, as well as a high degree of disintegratability in washing water.

The synthetic fibre chip or pulp may be Nylon, polyethylene etc and may have an average length between 100 and 500 µm and a fineness of 0.05 to 0.7 denier.

The granulated product may be coated with a waxy material and further coated with a finely divided colourant.

A QG / 197 85

**SPECIFICATION****Enzyme-granulating Method and Granular Composition Containing Enzyme****Field of the Invention**

5 The present invention relates to a method for granulating an enzyme and a granulated enzyme product thereof.

**Background of the Invention**

Granulated enzyme products are extensively used  
10 in the detergent, food, medical, leather and textile industries, as well as in the production of processed marine products, and a variety of commercial products suitable for specific purposes are available.

15 A granulated enzyme has the following advantages over an enzyme powder: 1) high flowability, 2) ease of measuring, 3) no sticking to the walls of a container, 4) no formation of agglomerates, 5) improved appearance, and 6) high 20 stability. If a granulated enzyme is used in a medicine or detergent, it must meet additional requirements such that it should easily disintegrate in liquids and have sufficient strength to withstand the usual handling of granules.

25 Conventional enzyme granules are produced by charging a mixture of an enzyme powder and water into a granulator, and granulating the powder either in the presence or in the absence of a binder etc. During the granulation, the charged mixture will 30 stick to the walls of the granulator, and the resulting deposit is not only undesirable from a hygienic viewpoint but it also causes problems in the carrying out of the granulation of the powder smoothly. A method of avoiding this problem, by 35 using a properly adjusted amount of water, is effective only in a limited range, and it often occurs that granules grow too fast to enable precise control over the granule size.

It is known that fibrous cellulose is used as an 40 ingredient for a granular composition containing an enzyme to improve granulation characteristics, as described in U.S. Patent 4,106,991. However, the resulting granular composition is still fragile and insufficient in toughness against fracture. Further, 45 as the content of enzyme in the granular composition is increased, it becomes more difficult to avoid sticking of the charged mixture to the walls of the granulator, and therefore it is necessary to add a very large amount of fibrous cellulose in the 50 composition in order to minimize sticking.

**Summary of the Invention**

One object of the present invention is to provide a granular composition containing an enzyme, particularly one suitable for use in detergents, the 55 granular composition (hereinafter sometimes referred to as "enzyme granules") not only having an improved stability and enhanced strength, but also exhibiting a high degree of disintegrability in washing water.

60 Another object of the invention is to provide a method for granulating an enzyme that solves all the problems associated with the use of an enzyme

in conventional detergents, and which is capable of producing enzyme granules that are attractive, 65 uniform in size, and highly flowable.

A further object of the present invention is to provide a process for preparing enzyme granules that ensures a smooth granulating operation without sticking on the walls of the granulator, and 70 which is capable of producing stabilized enzyme granules with a uniform size that may be provided with an attractive color if desired.

In accordance with the present invention, a composition consisting essentially of from 1 to 35% 75 by weight of an enzyme and from 0.5 to 30% by weight of synthetic fiber chip or pulp, with the balance being an extender or filler, is supplied to a granulator, and the composition is shaped into granules and dried.

**80 Detailed Description of the Invention**

Enzymes which can be used in the present invention include those commonly used in the detergent and other aforementioned industries, such as amylase, lipase, protease and cellulase, but 85 the present invention is not limited thereto and any enzymes derived from microorganisms, for example, Genus *Bacillus*, *Streptomyces*, and *Aspergillus* can be used. The enzyme may be used either in a dry form or as an aqueous solution. They

90 may be used alone or in combination. The amount of enzyme is from 1 to 35% by weight and preferably from 4 to 20% by weight. An alkaline protease API-21, derived from genus *Bacillus* sp. nov. NKS-21 which is described in U.S. Patent 95 4,480,037 and which has been deposited since Feb. 3, 1982 in the Fermentation Research Institute (FERM) in Japan as *Bacillus* sp. FERM BP-93, is an example of the protease.

In accordance with the present invention, enzyme 100 granules of improved strength and disintegrability can be obtained by granulating an enzyme together with a fine synthetic fibrous material in a form of chip or pulp. One particular advantage of synthetic fibers is that they provide 105 good lubricity during the working in a granulator, and therefore they are dispersed sufficiently to provide efficient granulation and produce enzyme granules of a satisfactory strength and a good disintegrability.

110 Preferred examples of synthetic fibers include Nylon, polyethylene, polypropylene, vinylon, polyester and acrylic fibers, which have an average fiber length of from 100 to 500 µm and a fiber fineness of from 0.05 to 0.7 denier, preferably from

115 0.3 to 0.5 denier. The synthetic fiber is incorporated in an amount of from 0.5 to 30% by weight and preferably from 2 to 20% by weight. Vinylon fibers with a fineness of 0.53 denier can be chopped to a fiber length of 0.3 mm by a dry cutting method, and 120 such chopped vinylon fibers of fiber lengths of from 0.3 to 0.5 mm are preferably used in the present invention.

The remainder of the composition is an extender or filler. Extenders or fillers suitable for use in the 125 present invention include water-soluble or -dispersible inorganic salts of alkali metals and

alkaline earth metals such as Na, K, Mg and Ca. For example, sodium sulfate, sodium chloride, calcium sulfate and calcium carbonate are used as extenders or fillers for enzyme granules suitable for detergent compositions.

The composition of the present invention may further contain a suitable additive such as binder, granulation aid, colorant, stabilizer or reinforcing agent, which are conventionally used in the fields of 10 granulation and enzyme preparations. For instance, the feed composition preferably includes at least two of binder, granulation aid, reinforcing agent and colorant.

Preferred binders are viscous hydrophilic 15 materials commonly used in the field of granulation, and they include polyvinylpyrrolidone, polyvinylalcohol, and cellulose derivatives such as hydroxypropyl cellulose, methyl cellulose and carboxymethyl cellulose (CMC). These binders are 20 generally introduced in the composition as aqueous solutions, but, if desired, binders may be replaced by the sole use of water.

A granulation aid suitable for use in the present 25 invention can be water, or any of the waxy materials that have melting points in the range of from 30 to 70°C and which are used either as aqueous solutions or dispersions, or in a molten state. The granulation aid is optionally incorporated in an amount as necessary to have good granulation performance 30 and preferably of from 8 to 18% by weight based on the weight of the composition of the present invention. Typical granulation aids include polyethylene glycol, ethoxylated aliphatic alcohol, polyethylene glycol monooleate, and aliphatic acid 35 monoethanolamide. Water and/or waxy materials are used as granulation aids, and they contribute to the formation of granules whether they are used alone or in combination.

Colorants suitable for use in the present invention 40 can be any pigments. For example, TiO<sub>2</sub> and/or CaCO<sub>3</sub> optionally with SiO<sub>2</sub> are used as colorants for enzyme granules suitable for detergent compositions.

In the present invention, a mechanical stirring 45 mixer, mixer-type granulator, drum granulator and any other types of granulators may be used, with those mixer blades and/or chopper blades being preferred.

The granulation is generally carried out at a 50 temperature of from 10 to 50°C, preferably from 25 to 40°C, and the components of the feed composition may be supplied into the granulator in any order. Typically, the dry components such as enzyme, synthetic fiber and extender/filler are 55 supplied first, and then optional liquid binder and/or granulation aid (i.e., water and/or waxy material) is sprayed into the granulator through a nozzle.

Subsequently the enzyme granules obtained by this 60 procedure are dried in a dryer such as fluidized bed dryer. The dried granules usually have diameters in the range of from 0.1 to 2 mm.

By the method of the present invention, smooth-surfaced enzyme granules can be efficiently 65 obtained without any sticking or deposition of the feed composition on the walls of the granulator, and

this effect is assumed to result largely from the use of synthetic fiber chip or pulp.

The use of synthetic fiber chip or pulp also contributes to the formation of enzyme granules 70 which have good shape retention and wear-resistant properties, so that the method of the invention can be implemented to reduce the formation of dust particles and the occurrence of fractured granules to very low levels. In addition, the 75 synthetic fiber chip or pulp swells by absorbing water, and thus provides enzyme granules having good disintegrability.

According to one preferred embodiment of the present invention, the dried granules obtained by 80 the aforementioned procedure are supplied into a heated mixer at a temperature of from 20 to 120°C, preferably from 50 to 80°C, and then a meltable waxy material such as polyethylene glycol is supplied and mixed with the granules, so that the 85 granules are smoothly coated with the molten wax. Further a finely divided colorant comprising TiO<sub>2</sub>, and/or CaCO<sub>3</sub>, optionally with SiO<sub>2</sub>, is supplied into the mixer and mixed with the granules and thereafter the coated and colored granules thus 90 obtained are cooled if necessary, whereby enzyme granules having smoothly coated and white-colored surfaces which prevent dust formation from the granules can be obtained.

The following examples are provided to further 95 illustrate the present invention, but should not be taken as limiting the scope of the invention.

#### EXAMPLE 1

A granulator (LMA-10 of Nara Kikai K.K.) was supplied with 1,080g of ground sodium sulfate, 330g 100 of protease powder (API-21), 60g of vinylon chips (0.53 denier in fineness and 0.3 mm in length) and 30g of titanium dioxide, and the components supplied were mixed together by mixer blades and chopper rotary blades rotating at 200 rpm and 3,000 105 rpm, respectively, for 3 minutes.

While the mixer blades and chopper blades were rotating at the speeds indicated above, 200g of a 1% aqueous CMC solution was sprayed into the granulator through a air-atomizing nozzle, and the 110 mixing of the components was continued for an additional 12 minutes with the rotational speed of the mixer blades increased to 350 rpm. As a result, enzyme granules which are from spherical to ellipsoidal in shape and of a narrow size distribution 115 were obtained.

The granules were fed into a fluidized bed dryer where they were dried to a water content of 3% or less.

The dried granules had the following size 120 (average diameter) distribution:

Over 1.4 mm	13.6%
From 0.35 to 1.4 mm	86.2%
Under 0.35 mm	0.2%

#### COMPARATIVE EXAMPLE 1

The procedure of Example 1 was repeated, except 125

that no fiber chips were used. The resulting granules had very uneven surfaces and were accompanied by the extensive formation of fines.

Details of Comparative Example 1 are as follows.

- 5 A granulator (Model LMA-10 of Nara Kikai K.K.) was charged with 1,050g of ground sodium sulfate, 340g of protease powder (API-21), and 30g of titanium dioxide, and the components supplied were mixed together by mixer blades and chopper rotary blades 10 rotating at 200 rpm and 3,000 rpm, respectively, for 3 minutes. While the mixing was continued under the same conditions, a 1% aqueous CMC solution was sprayed into the granulator through a air-atomizing nozzle, and the mixture was subjected to 15 a 10-minute agitation.

Thereafter, the mixing was continued for an additional 12 minutes with the mixer blades rotating at 350 rpm.

- 20 The resulting granules were ellipsoids with uneven surfaces. They were fed into a fluidized bed dryer where they were dried to a water content of 3% or less. The dried granules had the following size distribution:

	Over 1.4 mm	19.0%
25	From 0.35 to 1.4 mm	58.0%
	Under 0.35 mm	23.0%

#### EXAMPLE 2

- The procedure of Example 1 was repeated, except that the granulator was supplied with 1,440g of 30 ground sodium sulfate, 440g of enzyme powder (API-21), 80g of vynylon chips (0.53 denier in fineness and 0.3 mm in length), and 40g of titanium dioxide. The resulting enzyme granules were from spherical to ellipsoidal in shape and from light gray 35 to white in color, and they had smooth surfaces without fiber projections.

#### EXAMPLE 3

- The procedure of Example 1 was repeated, except that the granulator was supplied with 1,520g of 40 ground sodium sulfate, 360g of enzyme powder (API-21), 80g of vynylon chips (0.53 denier in fineness and 0.3 mm in length), and 40g of titanium dioxide.

#### EXAMPLE 4

- 45 The procedure of Example 1 was repeated, except that the granulator was supplied with 1,200g of ground sodium sulfate, 360g of enzyme powder (API-21), 400g of synthetic pulp (polyethylene fibers with an average diameter of 50  $\mu\text{m}$  and length of 0.1 50 mm), and 40g of titanium dioxide.

#### COMPARATIVE EXAMPLE 2

- The procedure of Example 1 was repeated, except that the granulator was supplied with 1,400g of 55 ground sodium sulfate, 360g of enzyme powder (API-21), 200g of cellulose fibers (average diameter of 30  $\mu\text{m}$  and length of 0.15 mm), and 40g of titanium dioxide.

#### Fracture Test

Each of the granular enzyme samples prepared in

- 60 Examples 3 and 4, and Comparative Examples 1 and 2 was passed through two Tyler sieves (12 mesh and 48 mesh) to obtain granules of sizes in the range of from 0.3 to 1.4 mm. Two hundred grams of each of the sieved enzyme samples was charged into a 65 stainless steel ball mill (ID: 100 mm, L: 150 mm) together with 200g of steel balls (0.25 inch in diameter), and was ground at 100 rpm for 30 minutes. Each of the ground samples was recovered from the ball mill and passed through two Tyler 70 sieves (12 mesh and 48 mesh), and the portion that passed through the 48-mesh sieve was collected. The strength of each enzyme sample was determined by calculating the percentage of granules fractured (a) in the ball milled samples as follows:

$$75 \quad \text{Percentage of granules fractured in ball mill} = \frac{W}{200} \times 100 (\%),$$

wherein W is the weight in grams of the granules 80 passing through the 48-mesh sieve.

The data obtained are shown below.

Percentages of granules fractured in ball mill (a)		
Example 3	Vynylon chips	2.4%
85 Example 4	Synthetic pulp (polyethylene)	6%
Comparative Example 2	Cellulose fibers	10%
90 Comparative Example 1	No fibers	65%

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made 95 therein without departing from the spirit and scope thereof.

#### CLAIMS

1. A method for granulating an enzyme, which comprises supplying a granulator with a feed composition consisting essentially of from 1 to 35% by weight of an enzyme and from 0.5 to 30% by weight of a synthetic fiber chip or pulp, with the balance being an extender or filler, shaping the supplied feed composition into granules and drying said granules.
- 100 2. A method according to claim 1, wherein said synthetic fiber chip or pulp has an average length in the range of from 100 to 500  $\mu\text{m}$  and a fineness in the range of from 0.05 to 0.7 denier.
- 105 3. A method according to claim 1, wherein said enzyme is selected from the group consisting of amylase, lipase, protease and cellulase.
- 110 4. A method according to claim 3, wherein said enzyme is a protease.

5. A method according to claim 4, wherein said protease is API-21 derived from genus *Bacillus*.
6. A method according to claim 1, wherein said granules are further coated with a molten waxy material.
7. A method according to claim 6, wherein said coated granules are further coated with a finely divided colorant.
8. A method according to claim 7, wherein said colorant is  $TiO_2$ .
9. A method according to claim 6, wherein said molten waxy material is polyethylene glycol.
10. A granular composition consisting essentially of from 1 to 35% by weight of an enzyme and from 0.5 to 30% by weight of a synthetic fiber chip or pulp, with the balance being an extender or filler.
11. A granular composition according to claim 10, wherein said synthetic fiber chip or pulp has an average length in the range of from 100 to 500  $\mu m$  and a fineness in the range of from 0.05 to 0.7 denier.
12. A granular composition according to claim 10, wherein said enzyme is selected from the group consisting of amylase, lipase, protease and cellulase.
13. A granular composition according to claim 12, wherein said enzyme is a protease.
14. A granular composition according to claim 13, wherein said protease is API-21 derived from genus *Bacillus*.
15. A granular composition according to claim 10, wherein said granular composition is further coated with a molten waxy material.
16. A granular composition according to claim 15, wherein said coated granular composition is further coated with a finely divided colorant.
17. A granule composition according to claim 16, wherein said colorant is  $TiO_2$ .
18. A granular composition according to claim 15, wherein said molten waxy material is polyethylene glycol.

Printed for Her Majesty's Stationery Office by Courier Press, Leamington Spa. 6/1986. Demand No. 8817356.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.